Detection of Low Levels of Carbaryl in Food Using Agilent LC/MSD Trap System

Application Note

Environmental

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Introduction

Pesticides in food and beverages can be a significant route to human exposure. Extracts of composite food samples typically contain many compounds, which produce interfering compounds at the retention time of interest. This note describes the application of ion trap LC/MS/MS to determine pesticide and herbicide contamination in food samples.

The specific determination of the carbamate pesticide "carbaryl" in composite food extracts that represent typical meals have previously been investigated using a fluorescence technique.[1–3] However, the fluorescence method has drawbacks related to: (1) time consuming post-column derivatization, (2) false positives due to lack of specificity, (3) long sample preparation, (4) insufficient limits of detection, and (5) the lack of confirmatory information from the analytical results.

The goal of this method was to develop a confirmation assay to detect carbaryl in foods at low ng/g levels. Absolute confirmation, identification and quantification of the low levels of carbaryl can be acheived with the LC/MSD Trap primarily due to the high sensitivity and specificity of MS/MS with the ion trap.

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Experimental

Pesticides in food and beverages are considered a significant route for human exposure. To better assess exposure from dietary intake, whole food samples were collected over a 24-hour period, homogenized using a 5-gallon blender, and then analyzed as a composite sample. Aliquots of the homogenate were extracted using a nine step scheme: (1) acid precipitation using zinc acetate, (2) drying with potassium oxalate and (3) sodium sulfate, (4) soxhlet extraction, (5) solvent exchange, (6) liquid-liquid extraction followed by (7) GPC cleanup with a (8) final solvent exchange and (9) concentration into acetonitrile.

Table 1 lists the HPLC method used for the determination of carbaryl in food extracts.

Table 1. LC Conditions.

LC column:	4.6 X 250 mm Zorbax XDB-C_8
Mobile phase:	A = 95% H_2O: 5% ACN, 0.1M NH_4Ac, 0.1% CH_3COOH B = 40% H_2O: 60% ACN, 0.1 NH_4Ac, 0.1% CH_3COOH
Gradient program:	20% B for 10 minutes; ramp up to 100% B over 30 minutes; hold for a further 11 minutes at 100% B
Flowrate:	1 mL/min

LC/MS/MS was performed using an Agilent LC/MSD Trap mass spectrometer in the MS/MS full scan mode. Carbaryl was detected using positive ion electrospray, in which MS/MS was used to provide additional fragmentation information needed to confirm the presence of carbaryl.

Results and Discussion

Extracts of composite food samples typically contain many compounds (Figure 1) which produce interfering compounds at the retention time of interest. This LC/MS/MS positive ion electrospray method for carbaryl proved 20–30 times more sensitive compared to data acquired from a scanning instrument, such as a single quadrupole, enabling the detection of non-target compounds in the food extract. The selectivity offered by MS/MS enabled the detection of the carbaryl product ion at *m/z* 145 (Figure 2) generated from the $[M+H]^+$ ion of carbaryl. The subsequent quantitative analysis was performed using this product ion at *m/z* 145.

The limit of detection in this food matrix was found to be 1 ng/g and the limit of quantitation (LOQ) used for the determination in food was 10 ng/g, exhibiting a signal-to-noise of 40:1 in the composite food matrix (Figure 3). A calibration based on the *m/z* 145 product ion was linear (linear correlation coefficient of 0.994) over the concentration range of 1–1000 ng/g (Figure 4). When the Limit of Quantitation of the carbaryl for both techniques were compared, the LC/MS/MS was shown to be 12 times more sensitive than the HPLC fluoresence technique. The LOQ for LC/MS/MS was found to be 1–10 ng/g while the LOQ for the fluoresence was 120 ng/g.

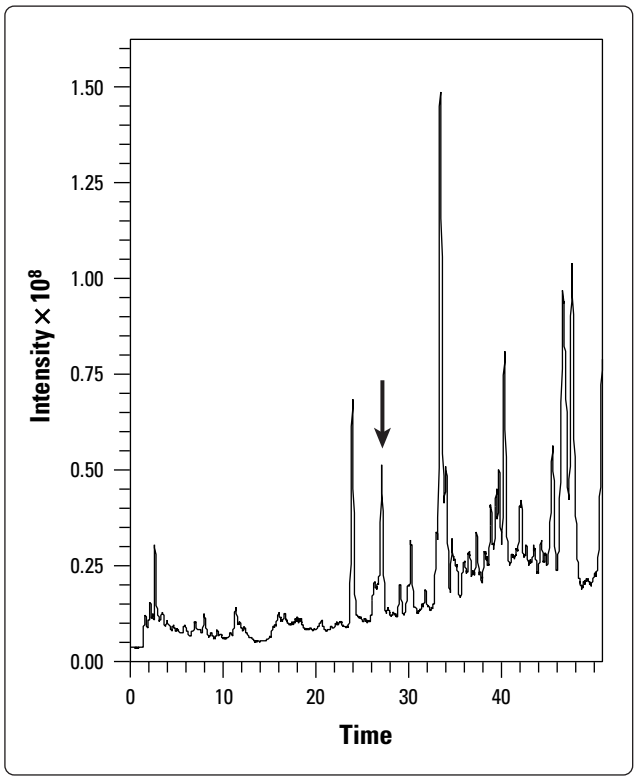

Figure 1. HPLC/ion trap MS full scan determination of carbaryl (retention time of carbaryl shown by arrow) in a composite food sample.

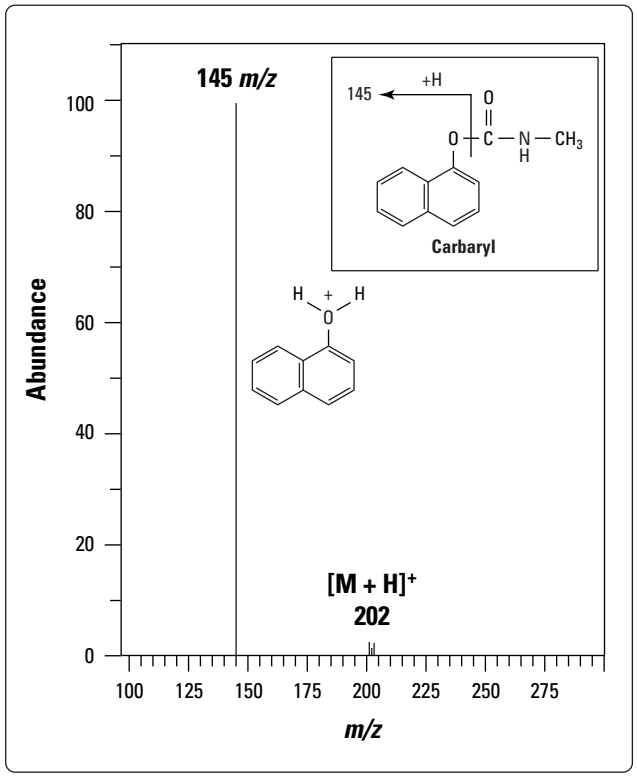

Figure 2. HPLC/MS/MS spectrum of carbaryl from Figure 1. The product ion spectrum was generated by mass selecting the $[M+H]^+$ ion at *m/z* 202 for collision induced decomposition using an end cap fragmentation voltage of 0.9V for 20 ms.

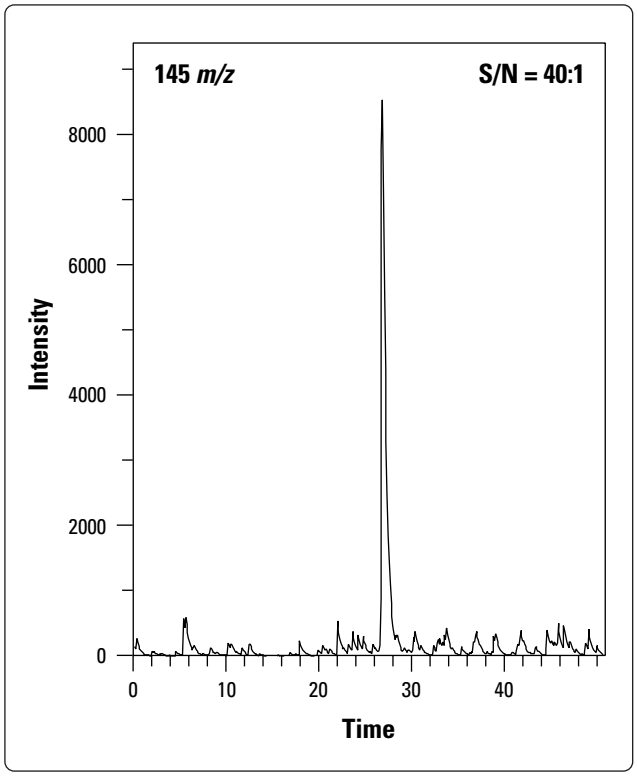

Figure 3. Ion trace of the carbaryl product ion at *m/z* 145 at the limit of quantitation LOQ (10 ng/g) in food.

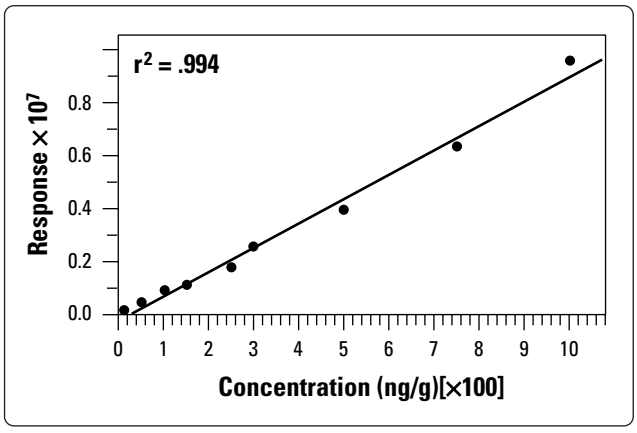

Figure 4. Calibration curve based on the *m/z* 145 product ion for carbaryl over the concentration range of 1–1000 ng/g.

The LC/MS/MS ion trap method confirmed that there were false positives in samples having a positive carbaryl identification by HPLC fluorescence (5 µg/g of carbaryl). The coeluting interference that also underwent post column derivatization, was a different molecular weight (*m/z* 213 vs 201 for carbaryl) and showed a different product ion spectrum (Figure 5), compared to carbaryl (Figure 2). Based on the MS/MS spectrum of the interference, a possible structure could be assigned as shown in Figure 5.

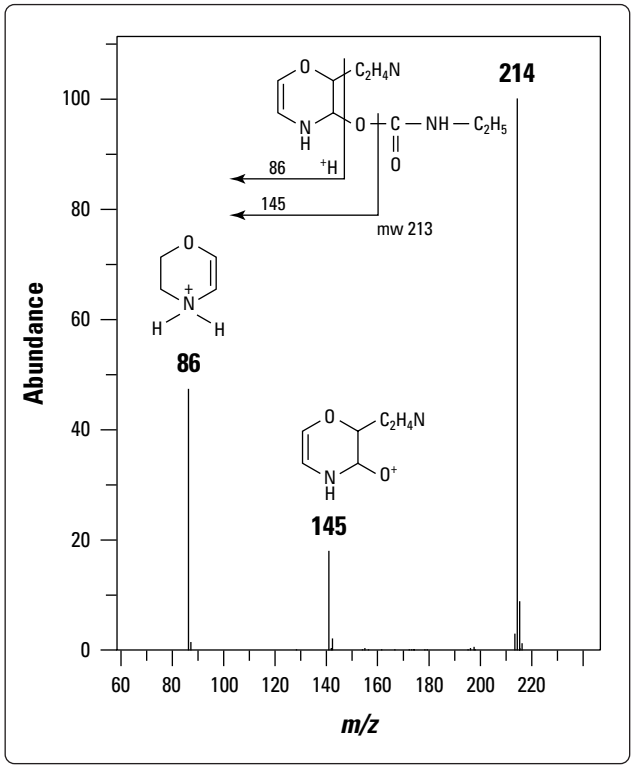

Figure 5. HPLC/MS/MS spectrum of the coeluting interference that produced a false positives in the HPLC fluorescence method.

Conclusions

This application has shown that the analysis of food samples for pesticides/herbicides using ion trap MS/MS detection can be accomplished successfully. This method allows for the detection, confirmation and quantitation of the carbamate pesticide carbaryl in extracts of whole food samples down to 1 ng/g levels.

References

1. Forest, D. L., U. S. Environmental Protection Agency, Method 531.1. *Measurement of N-Methylcarbamoyloximes and N-Methylcarbamates in Water by Direct Aqueous Injection HPLC with Post Column Derivatization*, Revision 1.0 (1985).
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